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Peer Review File

Ultrafast Switching and High-Endurance Nonvolatile Memory Enabled by Intrinsic Switchable Polarization in Semiconducting Janus Monolayers

Corresponding Author: Professor Seong Chu Lim

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
With this revised version, most comments and suggestions have been addressed to a high standard.

However, I share the remaining concerns raised by referee #3 regarding the strength of the claims about the ferroelectric behaviour of the investigated Janus MoSSe monolayers.

Regarding the PFM results, in my view, the absence of a clear 180° phase switching significantly weakens the claim of genuine ferroelectric polarization switching. Without a full phase reversal, it is difficult to rule out alternative origins such as electrostatic effects or piezoelectric-like responses. Moreover, in ultrathin Janus monolayers, the electrical signal from the measurement circuitry itself can be strongly coupled to the sample response, making it challenging to cleanly separate intrinsic piezoelectric or ferroelectric behavior from instrumental artifacts. In this context, crosstalk between the measurement system and the sample cannot be excluded and should be addressed more explicitly.

With respect to the in-situ biasing Raman measurements, the reported changes in peak position and linewidth do not clearly correlate with the voltage values at which electrical switching is claimed to occur. The observed spectral variations alone are therefore insufficient to directly support the conclusion that the electrical behavior originates from ferroelectric switching. In my opinion, the current Raman data do not provide unambiguous evidence of a hysteretic ferroelectric response.

Based on these considerations, I believe the authors should either (i) provide a much clearer and more rigorous explanation of the underlying physical mechanism linking the electrical characteristics to ferroelectricity, supported by more definitive experimental evidence, or (ii) consider removing the term “Ferroelectric” from the title “Ferroelectric Janus Monolayers” and revising the manuscript accordingly to avoid overstating the claims.

Finally, there are still a few typographical errors that need to be corrected—for example, Fig. 4b is incorrectly labeled as Fig. 4c. Please carefully review the entire manuscript once more to ensure that no typos remain.

Reviewer #3

(Remarks to the Author)
Duong et al. report a semiconducting ferroelectric (SFe) transistor based on monolayer Janus MoSeS. The device exhibits an ultralow energy consumption of 113.9/89.8 fJ per program/erase cycle and fatigue-free endurance over 10^7 cycles. The manuscript provides a solid discussion of the growth of the Janus material, and the demonstrated device performance is promising. However, as a central claim of the work, the evidence supporting ferroelectricity requires more careful examination. The authors employ multiple approaches—such as cross-sectional STEM imaging, PFM, and in-situ biasing Raman spectroscopy—to attribute the device behavior to ferroelectricity in Janus MoSeS. Nevertheless, some of the

presented results do not unambiguously support the stated conclusions. I believe the manuscript could be suitable for publication in Nature Communications, provided that the following concerns are adequately addressed.
Questions
1) Consistency of the PFM results requires clarification. I appreciate the authors for adding substantial additional experiments. For the PFM evidence, although the single-point measurement in Fig. 2h shows a full 180° phase switching, the domain mapping in Supplementary Fig. 21 exhibits a maximum phase contrast of only ~100°, which is relatively small. For out-of-plane ferroelectric polarization, such incomplete phase reversal does not provide strong or self-consistent evidence of robust ferroelectric domain switching. The authors should provide a detailed explanation for this discrepancy.
2) The interpretation of the in-situ biasing Raman measurements should be revised. Based on Supplementary Fig. 20, it is difficult to conclude that the Raman peak position and linewidth of MoSeS exhibit clear hysteresis during gate-voltage sweeping. Except for the initial point of the voltage sweep, the curves largely overlap, particularly at Vg = 0 V. Therefore, I suggest that the authors remove or substantially revise the statements claiming a hysteretic Raman response, unless stronger evidence or more quantitative analysis can be provided.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
With the current revision, the authors have appropriately addressed the remaining concerns raised in the previous round of review regarding the PFM and Raman measurements. The manuscript is now acceptable for publication in its present form.

Reviewer #3

(Remarks to the Author)
I sincerely appreciate the authors' efforts in addressing my previous comments. I support the authors' decision to remove the term "ferroelectric" from the title. However, I strongly recommend that the authors systematically revise the Introduction section and the main texts about the claims of ferroelectric mechanisms that authors agree are not appropriate. Furthermore, I strongly encourage the authors to carefully review the content of the main text and substantially revise the Discussion section to better highlight the advantages of semiconducting Janus monolayer devices. For example, the claimed 7-bit synaptic operations are not mentioned or substantiated in the main text.

With this revised version, most comments and suggestions have been addressed to a high standard. However, I share the remaining concerns raised by referee #3 regarding the strength of the claims about the ferroelectric behavior of the investigated Janus MoSSe monolayers.

Response: We sincerely thank the reviewer for the careful reassessment of our revised manuscript and for recognizing that most concerns have been addressed to a high standard. We appreciate the remaining critical comments regarding the strength of the ferroelectric claim, particularly in relation to the PFM measurements and the in-situ biasing Raman data. Below, we respond point-by-point.

1. Regarding the PFM results, in my view, the absence of a clear 180° phase switching significantly weakens the claim of genuine ferroelectric polarization switching. Without a full phase reversal, it is difficult to rule out alternative origins such as electrostatic effects or piezoelectric-like responses. Moreover, in ultrathin Janus monolayers, the electrical signal from the measurement circuitry itself can be strongly coupled to the sample response, making it challenging to cleanly separate intrinsic piezoelectric or ferroelectric behavior from instrumental artifacts. In this context, crosstalk between the measurement system and the sample cannot be excluded and should be addressed more explicitly.

Response: We thank the reviewer for raising this important concern. We fully agree that, in classical bulk *insulating* ferroelectrics, robust 180° phase contrast in imaging-mode PFM is typically expected and is often interpreted as evidence of complete *out-of-plane* polarization reversal. We therefore appreciate the need to carefully address the reduced phase excursion observed in large area mapping.

In an ideal *insulating* ferroelectric, the displacement field is given by:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P},$$

where $\boldsymbol{P}$ is spontaneous polarization, $\boldsymbol{E}$ is external applied field, and $\varepsilon_0 = 8.854\times10^{-12}$ F/m (see e.g., A. K. Tagantsev et.al., *Domains in Ferroic Crystals and Thin Films* (Springer, 2010) or M. Dawber et.al., *Physics of thin-film ferroelectric oxides*, Rev. Mod. Phys. **77**, 1083 (2005)), whereas in *ferroelectric* semiconductors with a band gap (1.34 eV for Janus MoSeS), the external field can modulate the Fermi level and generate mobile charges. Thus, an additional free-carrier contribution must be included:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} + qn,$$

where q is an electrical charge and n is the free charge density. (see e.g., J. F. Scott, *Ferroelectric Memories*, Springer (2000)). The free carriers dynamically redistribute themselves and screen $\boldsymbol{P}$ induced from bound charges. As a result, the apparent response detected in imaging-mode PFM can be reduced, leading to weaker phase contrasts below 180° even when intrinsic polarization reversal.

This effect is amplified in ultrathin MoSeS (~0.7 nm), whose thickness lies within the electronic screening length (e.g., ~7 nm in multilayer MoS_2, *Nano Lett.* **13**, 3396 (2013)). Furthermore, imaging-mode PFM probes the quasi-static electromechanical response during slow raster scanning, allowing mobile carriers to redistribute and screen the polarization by bound charges. Therefore, the reduced phase contrast observed in large-area mapping reflects electronic screening and probe-geometry effects rather than incomplete polarization switching. We note that the incomplete phase reversal from imaging-mode PFM on various 2D ferroelectrics has been reported in the literature [e.g., *Science* **376,** 973–978 (2022), *Sci. Adv.* ***8,*** eabo0773 (2022), *Nat Commun* **14**, 8470 (2023), *Science* **372,** 1458–1462 (2021), and *Nat. Commun*. **12,** 53 (2021)]. In particular, Hu *et al.* [*Nat Commun* **14**, 8470 (2023)] explicitly observed incomplete 180° phase flipping during lithography box of writing and attributed this to factors such as tilted polarization orientation and limited dwell time. Zheng *et al.* [*Sci. Adv.* ***8,*** eabo0773 (2022)] demonstrated thickness-dependent stability of polar phases, highlighting that ultrathin layers may exhibit weaker or more complex polarization configurations.

Nevertheless, a complete switching of polarization is observable only when the characterization speed is swift enough because intrinsic polarization reversal occurs almost spontaneously. Importantly to note, local pulse-mode spectroscopy in our work still demonstrates full 180° phase switching, and quantitative PUND measurements further confirm a full switching behavior with equal and opposite remanent polarization in **Fig. 2h and j**. Therefore, the reduced phase contrast in large-area mapping reflects electronic screening and measurement geometry effects rather than incomplete polarization switching. We address the argument in Supplementary Note 5, shown below.

-Line 215,

'We employed two distinct PFM modes. The 180° phase switching in Fig. 2h was obtained using pulse-mode (off-field) spectroscopy, which probes the remanent electromechanical response and shows clear reversible switching with a butterfly-shaped amplitude loop, confirming bistable out-of-plane polarization. The reduced phase contrast observed in imaging-mode PFM arises from the different measurement geometry and electrostatic conditions. Janus MoSeS is a semiconducting ferroelectric monolayer in which polarization is coupled to mobile carriers; thus, the displacement field includes a free-carrier contribution (Supplementary Note 5) [41-43]. Under quasi-static raster scanning, mobile carriers can redistribute and partially screen bound polarization charges, reducing the apparent electromechanical response detected in imaging mode. This effect is enhanced in the ultrathin limit (~0.7 nm), where the entire layer lies within the electronic screening length. This effect has also been widely reported in other ultrathin 2D ferroelectrics and does not preclude intrinsic polarization switching when supported by independent electrical and spectroscopic evidence [44-45].'

References:

41. Tagantsev, A. K., Cross, L. E. & Fousek, J. *Domains in Ferroic Crystals and Thin Films* (Springer, New York, 2010).
42. Scott, J. F. *Ferroelectric Memories* (Springer, Berlin, 2000).
43. Dawber, M., Rabe, K. M. & Scott, J. F. Physics of thin-film ferroelectric oxides. *Rev. Mod. Phys.* **77**, 1083–1130 (2005).
44. Hu, Y., Rogée, L., Wang, W. *et al.* Extendable piezo/ferroelectricity in nonstoichiometric 2D transition metal dichalcogenides. *Nat. Commun.* **14**, 8470 (2023).
45. X. Zheng *et al.* Phase and polarization modulation in two-dimensional In_2Se_3 via in situ transmission electron microscopy. *Sci. Adv.* **8**, eabo0773 (2022).

Supplementary Note 5. PFM Analysis of Janus MoSeS Samples

1. Electrostatic Screening in Atomically Thin Semiconducting Ferroelectrics

In an ideal insulating ferroelectric, the electric displacement field $\boldsymbol{D}$ is given by $\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P}$, where ε_0 is vacuum permittivity, $\boldsymbol{P}$ denotes the polarization arising from bound charges, $\boldsymbol{E}$ is external applied field [25, 26]. However, in ferroelectric semiconductors with small band gap, the external field can modulate the electronic band and generate mobile charges. In this case, an additional free-carrier contribution must be included in displacement field:

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P} + qn,$$

where q is an electrical charge and n is the free charge density [27].

Janus MoSeS is an n-type semiconductor with a band gap of 1.34 eV. Under positive gate field, the conductance increases as shown in **Fig**. 1h and 1i. As a result, the apparent response detected in imaging-mode PFM can be affected by the changes in conductance. The free carriers dynamically redistribute themselves and screen $\boldsymbol{P}$ is induced from bound charges, leading to weaker phase contrast (i.e. smaller than 180°). These effects are particularly pronounced in atomically thin monolayers (~0.7 nm), where the entire body thickness lies within the electronic screening length. The Thomas–Fermi screening length can be approximated as:

$$\lambda_{\mathrm{TF}} \sim \sqrt{\frac{\varepsilon k_B T}{n q^2}},$$

for typical carrier densities in semiconducting 2D materials, is on order of several nanometer. In this regime, there is no "bulk" region electrically isolated from carriers, polarization and free carriers coexist within the same atomic layer, screening of bound charges is unavoidable and intrinsic.[10] Furthermore, imaging-mode PFM probes the quasi-static electromechanical response during relatively slow scanning. Under these conditions, mobile carriers have sufficient time to redistribute, partially screening the polarization associated with bound charges. Therefore, the reduced phase contrast observed in large-area mapping in **Supplementary Fig. 19** consists with electronic screening and probe-geometry effects, rather than incomplete polarization switching. We also note that the incomplete phase reversal from imaging-mode PFM has been reported in several studies of various 2D ferroelectrics [28-32].

Nevertheless, complete switching of polarization can be still observed when the characterization is performed on faster timescales, because intrinsic polarization reversal occurs nearly spontaneously. Importantly, local pulse-mode spectroscopy in our work still demonstrates full 180° phase switching. In addition, quantitative PUND measurements further confirm complete polarization reversal with equal and opposite remanent polarization in Fig. 2h and j. Therefore, the reduced phase contrast in large-area mapping primarily reflects electronic screening and measurement geometry effects, rather than incomplete polarization switching.

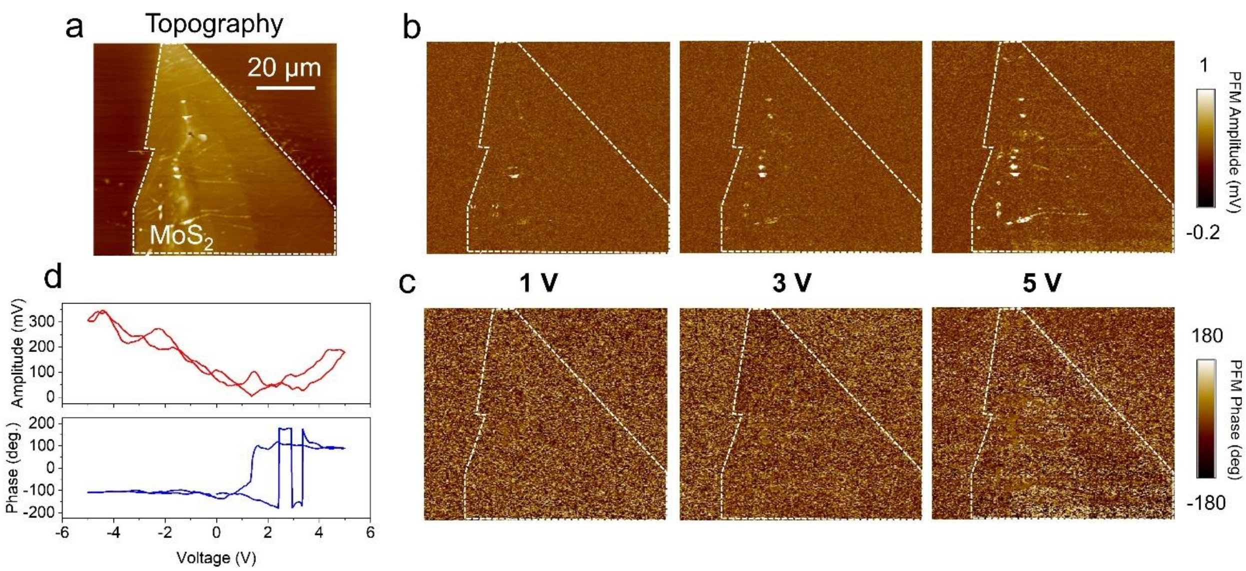
Response: Regarding important concern of possible measurement artifacts and crosstalk in ultrathin samples, we performed identical PFM measurements on a monolayer MoS_2 (control sample) fabricated on the same p^{++} Si substrate and measured under the same instrumental conditions (tip material, drive amplitude, frequency, and environmental parameters). Monolayer MoS_2 is a centrosymmetric and non-polar semiconductor and therefore is not expected to exhibit ferroelectric switching. As shown in Supplementary Fig. 20, MoS_2 displays no phase or amplitude contrast in imaging mode, no hysteresis in phase–voltage or amplitude–voltage curves, and no butterfly-shaped amplitude response. The absence of switching signatures that the phase contrast and hysteresis observed in Janus MoSeS are not due to instrumental crosstalk, capacitive coupling, or ultrathin-body artifacts. Instead, they arise from intrinsic properties of the Janus MoSeS monolayer.

-Line 213,

'Control measurements on monolayer MoS_2 confirm the absence of instrumental artifacts and measurement crosstalk during microscopy (Supplementary Fig 21).'

Supplementary Note 5. PFM Analysis of Janus MoSeS Samples

3. Control PFM of monolayer MoS_2



Supplementary Fig. 21. Control PFM of monolayer MoS_2. a, AFM topography of non-ferroelectric monolayer MoS_2. **b,** PFM amplitude, and **c**, phase maps under increasing drive bias from 1 V to 5 V. No discernible phase or amplitude contrast is observed, relative to the substrate. **d**, PFM amplitude– and phase–voltage spectroscopy of MoS_2, which was obtained under identical conditions to Janus MoSeS.

To further investigate the possibility of instrumental artifacts or capacitive crosstalk, we performed PFM on monolayer MoS_2 under the same experimental conditions (tip, drive amplitude, frequency, and environment). Monolayer MoS_2 is a centrosymmetric, non-ferroelectric semiconductor with similar thickness and n-type conduction to Janus MoSeS, making it an appropriate control to evaluate potential measurement artifacts.

As expected, monolayer MoS_2 shows neither hysteresis in the phase–voltage or amplitude–voltage curves nor a butterfly-shaped amplitude response, which are characteristic signatures of ferroelectric switching. The absence of these features confirms that the phase contrast and switching behavior observed in Janus MoSeS are not caused by instrumental crosstalk, capacitive coupling, or ultrathin-body artifacts. Instead, they originate from the intrinsic properties of the Janus MoSeS monolayer. (**Supplementary Fig. 21**).

2. With respect to the in-situ biasing Raman measurements, the reported changes in peak position and linewidth do not clearly correlate with the voltage values at which electrical switching is claimed to occur. The observed spectral variations alone are therefore insufficient to directly support the conclusion that the electrical behavior originates from ferroelectric switching. In my opinion, the current Raman data do not provide unambiguous evidence of a hysteretic ferroelectric response.

Response: We sincerely thank the reviewer for the insightful comments regarding the bias-dependent Raman measurements. After thorough discussions, we agree that the current bias-dependent Raman spectra are not comprehensive enough to provide conclusive evidence for ferroelectric switching. In this regards, we decided to **remove all bias-dependent Raman data from both the main text and the Supplementary Information**. As suggested by reviewer #3, these Raman results at present serve only as indicative, rather than definitive observations for ferroelectric switching.

Importantly, the demonstration of ferroelectricity in our study relies primarily on electrical measurements, including P–E hysteresis, and DFT calculations, which independently and consistently support polarization switching. Therefore, the conclusions of the manuscript remain unaffected without Raman data. We recognize that bias-dependent Raman spectroscopy is a powerful tool for probing polarization dynamics, and we plan to conduct a more systematic and quantitative investigation in future work to ensure sufficient statistical reliability and mechanistic clarity. We appreciate the reviewer's guidance, which has helped us improve the scientific rigor and clarity of the manuscript.

Supplementary Note 4. 4. Probing the atomic structure re-coordination using *in-situ* biasing Raman spectroscopy, and **Supplementary Figs. 19 and 20** were withdrawn from the revised Supplementary Information. Accordingly, the following statements were removed from the main text.

-Line 78,

'as confirmed by first-principles calculations, and cross-sectional STEM imaging. ~~and *in-situ* biasing Raman spectroscopy.~~'

-Line 194,

'as determined by normalizing the total energy of each ferroelectric switching pathway (Supplementary Fig. 17c). Moreover, *in-situ* bias-dependent Raman measurements uncovered that A_1' mode exhibits clear frequency hysteresis between forward and reverse gate voltage sweeps from -8V to +8 V (Supplementary Figs. 19, 20), suggesting that polarization switching from the upward to downward direction is partially suppressed under reverse bias. This hysteresis is consistent with the conductance behaviors observed in Fig. 1i. The hysteresis of A_1' phonons upon gate bias is related to the structure itself, rather than being influenced by the metal-MoSeS junction or trap sites. This asymmetric switching behavior is attributed to the broken symmetry of binding energies inherent in Janus structures. Such asymmetry-driven polarization dynamics are not typically observed in conventional sliding or bulk ferroelectric systems.'

3. Based on these considerations, I believe the authors should either (i) provide a much clearer and more rigorous explanation of the underlying physical mechanism linking the electrical characteristics to ferroelectricity, supported by more definitive experimental evidence, or (ii) consider removing the term "Ferroelectric" from the title "Ferroelectric Janus Monolayers" and revising the manuscript accordingly to avoid overstating the claims.

Response: We thank the reviewer for the thoughtful suggestion regarding the removal of the term 'ferroelectric' in the title. After consideration, we have revised the title to:

"Ultrafast Switching and High-Endurance Nonvolatile Memory Enabled by Intrinsic Switchable Polarization in Semiconducting Janus Monolayers"

This revised title avoids potential overstatement while accurately reflecting the central finding of intrinsic switchable polarization in Janus MoSeS and its role in enabling high-performance nonvolatile memory.

-The corresponding terminology has been updated throughout the revised manuscript and Supplementary Information to maintain consistency.

4. Finally, there are still a few typographical errors that need to be corrected—for example, Fig. 4b is incorrectly labeled as Fig. 4c. Please carefully review the entire manuscript once more to ensure that no typos remain.

Response: We thank the reviewer for carefully pointing out the typographical errors in the manuscript. We have thoroughly reviewed the entire manuscript and corrected the identified typos, as summarized below.

-Line 296,

‘Fig. 4b and Supplementary Fig 30’

-Line 320,

‘in Supplementary Fig. 31, and Fig. 4e’

-Line 211,

‘(Figs. 2f-h, and Supplementary Fig. 19)’

-Line 242,

‘in Fig. 2k’

Response to Reviewer 3

Duong et al. report a semiconducting ferroelectric (SFe) transistor based on monolayer Janus MoSeS. The device exhibits an ultralow energy consumption of 113.9/89.8 fJ per program/erase cycle and fatigue-free endurance over 10^7 cycles. The manuscript provides a solid discussion of the growth of the Janus material, and the demonstrated device performance is promising. However, as a central claim of the work, the evidence supporting ferroelectricity requires more careful examination. The authors employ multiple approaches—such as cross-sectional STEM imaging, PFM, and in-situ biasing Raman spectroscopy—to attribute the device behavior to ferroelectricity in Janus MoSeS. Nevertheless, some of the presented results do not unambiguously support the stated conclusions. I believe the manuscript could be suitable for publication in Nature Communications, provided that the following concerns are adequately addressed.

Response: We sincerely thank the reviewer for the thoughtful and constructive evaluation of our manuscript. We are grateful for the positive assessment of the material growth quality and device performance. We appreciate the reviewer's careful scrutiny of the central ferroelectric claim and address each concern below in detail.

Questions

1) Consistency of the PFM results requires clarification. I appreciate the authors for adding substantial additional experiments. For the PFM evidence, although the single-point measurement in Fig. 2h shows a full 180° phase switching, the domain mapping in Supplementary Fig. 21 exhibits a maximum phase contrast of only ~100°, which is relatively small. For out-of-plane ferroelectric polarization, such incomplete phase reversal does not provide strong or self-consistent evidence of robust ferroelectric domain switching. The authors should provide a detailed explanation for this discrepancy.

Response: We thank the reviewer for this important and thoughtful comment. We agree that consistency between local spectroscopy and large-area domain mapping is essential when evaluating ferroelectric switching.

In our study, two fundamentally different measurement modes were employed. The 180° phase switching shown in Fig. 2h was obtained using pulse-mode (off-field) PFM spectroscopy. This protocol probes the remanent electromechanical response rather than the field-driven response and is conceptually analogous to measuring remanent polarization in macroscopic P–E characterization. Under these conditions, Janus MoSeS exhibits reversible phase switching approaching 180°, accompanied by a butterfly-shaped amplitude response, indicating bistable out-of-plane polarization.

We fully agree that, in classical bulk *insulating* ferroelectrics, robust 180° phase contrast in imaging-mode PFM is typically expected and is often interpreted as evidence of complete *out-*

of-plane polarization reversal. We therefore appreciate the need to carefully address the reduced phase excursion observed in large area mapping.

In an ideal *insulating* ferroelectric, the displacement field is given by:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P},$$

where $\boldsymbol{P}$ is spontaneous polarization, $\boldsymbol{E}$ is external applied field, and $\varepsilon_0 = 8.854\times10^{-12}$ F/m (see e.g., A. K. Tagantsev et.al. *Domains in Ferroic Crystals and Thin Films* (Springer, 2010) or M. Dawber et.al., *Physics of thin-film ferroelectric oxides*, Rev. Mod. Phys. **77**, 1083 (2005)), whereas in ferroelectric semiconductors with small band gap, the external field can modulate the band and generate mobile charges. Thus, an additional free-carrier contribution must be included $\boldsymbol{D}$:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} + qn,$$

where q is an electrical charge and n is the free charge density. (see e.g., J. F. Scott, *Ferroelectric Memories*, Springer (2000)). The free carriers dynamically redistribute themselves and screen **P** induced from bound charges.

Janus MoSeS is an n-type semiconductor with a band gap of 1.72 eV. Under positive gate field, the conductance increases owing to the band modulation, as shown in Fig. 1h and 1i. As a result, the apparent response detected in imaging-mode PFM can be reduced, leading to weaker phase contrasts below 180° even when free carrier density increased. This effect is amplified when the screening is weak. The electronic screening length is order of several nm (e.g., ~7 nm in multilayer MoS_2, *Nano Lett.* **13**, 3396 (2013)). Furthermore, imaging-mode PFM probes the quasi-static electromechanical response during slow raster scanning, allowing mobile carriers to redistribute and screen the polarization by bound charges. Therefore, the reduced phase contrast observed in large-area mapping reflects electronic screening and probe-geometry effects rather than incomplete polarization switching. We note that the incomplete phase reversal from imaging-mode PFM on various 2D ferroelectrics has been reported in the literature [*Science* **376,** 973–978 (2022), *Sci. Adv.* ***8,*** eabo0773 (2022), *Nat Commun* **14**, 8470 (2023), *Science* **372,** 1458–1462 (2021), *Nat. Commun*. **12,** 53 (2021)].

Nevertheless, a complete switching of polarization is observable only when the characterization speed is swift enough because intrinsic polarization reversal occurs almost spontaneously. Importantly to note, local pulse-mode spectroscopy in our work still demonstrates full 180° phase switching, and quantitative PUND measurements further confirm a full switching behavior with equal and opposite remanent polarization in **Fig. 2h and j**. Therefore, the reduced phase contrast in large-area mapping reflects electronic screening and measurement geometry effects rather than incomplete polarization switching. We address the argument in Supplementary Note 5, shown below.

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'We employed two distinct PFM modes. The 180° phase switching in Fig. 2h was obtained using pulse-mode (off-field) spectroscopy, which probes the remanent electromechanical response and shows clear reversible switching with a butterfly-shaped amplitude loop, confirming bistable out-of-plane polarization. The reduced phase contrast observed in imaging-mode PFM arises from the different measurement geometry and electrostatic conditions. Janus MoSeS is a semiconducting ferroelectric monolayer in which polarization is coupled to mobile carriers; thus, the displacement field includes a free-carrier contribution (Supplementary Note 5) [41-43]. Under quasi-static raster scanning, mobile carriers can redistribute and partially screen bound polarization charges, reducing the apparent electromechanical response detected in imaging mode. This effect is enhanced in the ultrathin limit (~0.7 nm), where the entire layer lies within the electronic screening length. This effect has also been widely reported in other ultrathin 2D ferroelectrics and does not preclude intrinsic polarization switching when supported by independent electrical and spectroscopic evidence [44, 45].'

References:

41. Tagantsev, A. K., Cross, L. E. & Fousek, J. *Domains in Ferroic Crystals and Thin Films* (Springer, New York, 2010).

42. Scott, J. F. *Ferroelectric Memories* (Springer, Berlin, 2000).

43. Dawber, M., Rabe, K. M. & Scott, J. F. Physics of thin-film ferroelectric oxides. *Rev. Mod. Phys.* **77**, 1083–1130 (2005).

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45. X. Zheng *et al.* Phase and polarization modulation in two-dimensional In_2Se_3 via in situ transmission electron microscopy. *Sci. Adv.* **8**, eabo0773 (2022).

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1. Electrostatic Screening in Atomically Thin Semiconducting Ferroelectrics

In an ideal insulating ferroelectric, the electric displacement field $\boldsymbol{D}$ is given by $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}$, where ε_0 is vacuum permittivity, $\boldsymbol{P}$ denotes the polarization arising from bound charges, $\boldsymbol{E}$ is external applied field [25, 26]. However, in ferroelectric semiconductors with small band gap, the external field can modulate the electronic band and generate mobile charges. In this case, an additional free-carrier contribution must be included in displacement field:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} + qn,$$

where q is an electrical charge and n is the free charge density [27].

Janus MoSeS is an n-type semiconductor with a band gap of 1.34 eV. Under positive gate field, the conductance increases as shown in **Fig**. 1h and 1i. As a result, the apparent response detected in imaging-mode PFM can be affected by the changes in conductance. The free carriers dynamically redistribute themselves and screen $\boldsymbol{P}$ is induced from bound charges, leading to weaker phase contrast (i.e. smaller than 180°). These effects are particularly pronounced in atomically thin monolayers (~0.7 nm), where the entire body thickness lies within the electronic screening length. The Thomas–Fermi screening length can be approximated as:

$$\lambda_{\mathrm{TF}} \sim \sqrt{\frac{\varepsilon k_B T}{nq^2}},$$

for typical carrier densities in semiconducting 2D materials, is on order of several nanometer. In this regime, there is no "bulk" region electrically isolated from carriers, polarization and free carriers coexist within the same atomic layer, screening of bound charges is unavoidable and intrinsic.[10] Furthermore, imaging-mode PFM probes the quasi-static electromechanical response during relatively slow scanning. Under these conditions, mobile carriers have sufficient time to redistribute, partially screening the polarization associated with bound charges. Therefore, the reduced phase contrast observed in large-area mapping in **Supplementary Fig. 19** consists with electronic screening and probe-geometry effects, rather than incomplete polarization switching. We also note that the incomplete phase reversal from imaging-mode PFM has been reported in several studies of various 2D ferroelectrics [28-32].

Nevertheless, complete switching of polarization can be still observed when the characterization is performed on faster timescales, because intrinsic polarization reversal occurs nearly spontaneously. Importantly, local pulse-mode spectroscopy in our work still demonstrates full 180° phase switching. In addition, quantitative PUND measurements further confirm complete polarization reversal with equal and opposite remanent polarization in Fig. 2h and j. Therefore, the reduced phase contrast in large-area mapping primarily reflects electronic screening and measurement geometry effects, rather than incomplete polarization switching.

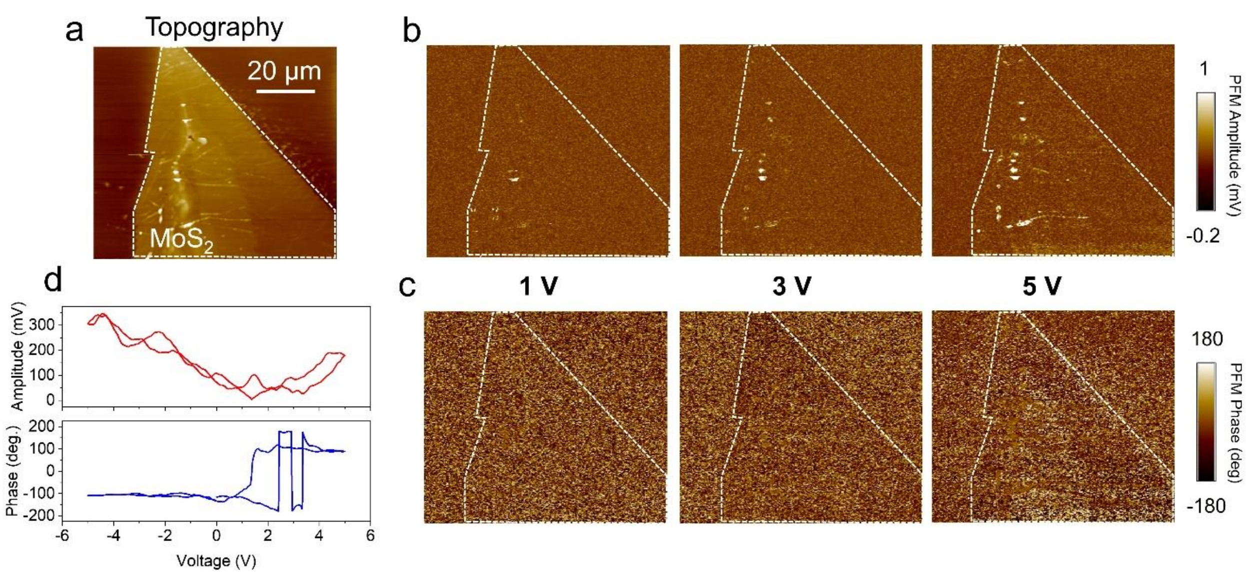
Response: Regarding important concern of possible measurement artifacts and crosstalk in ultrathin samples, we performed identical PFM measurements on a monolayer MoS_2 fabricated on the same p^{++} Si substrate and measured under the same instrumental conditions (tip material, drive amplitude, frequency, and environmental parameters). Monolayer MoS_2 is a centrosymmetric and non-polar semiconductor and therefore is not expected to exhibit ferroelectric switching. As shown in Supplementary Fig. 20, MoS_2 displays no phase or amplitude contrast in imaging mode, no hysteresis in phase–voltage or amplitude–voltage curves, and no butterfly-shaped amplitude response. The absence of switching signatures that the phase contrast and hysteresis observed in Janus MoSeS are not due to instrumental crosstalk, capacitive coupling, or ultrathin-body artifacts. Instead, they arise from intrinsic properties of the Janus MoSeS monolayer.

-Line 213,

'Control measurements on monolayer MoS_2 confirm the absence of instrumental artifacts and measurement crosstalk during microscopy (Supplementary Fig 21).'

Supplementary Note 5. PFM Analysis of Janus MoSeS Samples

3. Control PFM of monolayer MoS_2



Supplementary Fig. 21. PFM of monolayer MoS_2. a, AFM topography of non-ferroelectric monolayer MoS_2. **b,** PFM amplitude, and **c**, phase maps under increasing drive bias from 1 V to 5 V. No discernible phase or amplitude contrast is observed, relative to the substrate. **d**, PFM amplitude– and phase–voltage spectroscopy of MoS_2, which was obtained under identical conditions to Janus MoSeS.

To further investigate the possibility of instrumental artifacts or capacitive crosstalk, we performed PFM on monolayer MoS_2 under the same experimental conditions (tip, drive amplitude, frequency, and environment). Monolayer MoS_2 is a centrosymmetric, non-ferroelectric semiconductor with similar thickness and n-type conduction to Janus MoSeS, making it an appropriate control to evaluate potential measurement artifacts.

As expected, monolayer MoS_2 shows neither hysteresis in the phase–voltage or amplitude–voltage curves nor a butterfly-shaped amplitude response, which are characteristic signatures of ferroelectric switching. The absence of these features confirms that the phase contrast and switching behavior observed in Janus MoSeS are not caused by instrumental crosstalk, capacitive coupling, or ultrathin-body artifacts. Instead, they originate from the intrinsic properties of the Janus MoSeS monolayer. (**Supplementary Fig. 21**).

2) The interpretation of the in-situ biasing Raman measurements should be revised. Based on Supplementary Fig. 20, it is difficult to conclude that the Raman peak position and linewidth of MoSeS exhibit clear hysteresis during gate-voltage sweeping. Except for the initial point of the voltage sweep, the curves largely overlap, particularly at $V_g = 0$ V. Therefore, I suggest that the authors remove or substantially revise the statements claiming a hysteretic Raman response, unless stronger evidence or more quantitative analysis can be provided.

Response: We sincerely thank the reviewer for the insightful comments regarding the bias-dependent Raman measurements. After thorough discussions, we agree that the current bias-dependent Raman spectra are not comprehensive enough to provide conclusive evidence for ferroelectric switching. In this regards, we decided to **remove all bias-dependent Raman data from both the main text and the Supplementary Information**. As suggested by reviewer #3, these Raman results at present serve only as indicative, rather than definitive observations for ferroelectric switching.

Importantly, the demonstration of ferroelectricity in our study relies primarily on electrical measurements, including P–E hysteresis, and DFT calculations, which independently and consistently support polarization switching. Therefore, the conclusions of the manuscript remain unaffected without Raman data. We recognize that bias-dependent Raman spectroscopy is a powerful tool for probing polarization dynamics, and we plan to conduct a more systematic and quantitative investigation in future work to ensure sufficient statistical reliability and mechanistic clarity. We appreciate the reviewer's guidance, which has helped us improve the scientific rigor and clarity of the manuscript.

Supplementary Note 4. 4. Probing the atomic structure re-coordination using *in-situ* biasing Raman spectroscopy, and **Supplementary Figs. 19 and 20** were withdrawn from the revised Supplementary Information. Accordingly, the following statements were removed from the main text.

-Line 78,

'as confirmed by first-principles calculations, and cross-sectional STEM imaging. ~~and *in-situ* biasing Raman spectroscopy.~~'

-Line 194,

'as determined by normalizing the total energy of each ferroelectric switching pathway (Supplementary Fig. 17c). ~~Moreover, *in-situ* bias-dependent Raman measurements uncovered that A_1' mode exhibits clear frequency hysteresis between forward and reverse gate voltage sweeps from -8V to +8 V (Supplementary Figs. 19, 20), suggesting that polarization switching from the upward to downward direction is partially suppressed under reverse bias. This hysteresis is consistent with the conductance behaviors observed in Fig. 1i. The hysteresis of A_1' phonons upon gate bias is related to the structure itself, rather than being influenced by the metal-MoSeS junction or trap sites.~~ This asymmetric switching behavior is attributed to the broken symmetry of binding energies inherent in Janus structures. Such asymmetry-driven polarization dynamics are not typically observed in conventional sliding or bulk ferroelectric systems.'

We hope that the revisions satisfactorily address all concerns and respectfully submit the revised version for your consideration.

Sincerely,

Seong Chu Lim

On behalf of all authors

Response to Reviewer 3

I sincerely appreciate the authors' efforts in addressing my previous comments. I support the authors' decision to remove the term "ferroelectric" from the title. However, I strongly recommend that the authors systematically revise the Introduction section and the main texts about the claims of ferroelectric mechanisms that authors agree are not appropriate. Furthermore, I strongly encourage the authors to carefully review the content of the main text and substantially revise the Discussion section to better highlight the advantages of semiconducting Janus monolayer devices. For example, the claimed 7-bit synaptic operations are not mentioned or substantiated in the main text.

Response: We sincerely thank the reviewer for the constructive feedback and for supporting the revision of the title. Following the reviewer's suggestion, we have carefully revised the Introduction and main text to ensure consistent and precise terminology. Specifically, statements referring to "ferroelectric mechanisms" have been moderated and aligned with the concept of **intrinsic switchable polarization**, avoiding overstatement while preserving the physical interpretation supported by our experimental results.

We have substantially revised the **Discussion**, inside which we have emphasized the device-level not only (i) superior performance of semiconducting Janus MoSeS for ultrafast switching, low-power operation, but also (ii) advantages of scalability and compatibility within the present field-effect transistor architectures, comparing to the other 2D layered ferroelectric materials. In addition, (iii) we moderated the discussion of switching mechanisms by explicitly acknowledging that further investigation is required to fully elucidate their microscopic origin. These revisions provide a more concise and balanced presentation of the key findings.

Importantly, as requested by the editor, we have added a statement in the manuscript to acknowledge that further work is required to fully establish the microscopic switching mechanisms:

-line 370,

While the primary focus of this work remains the switching polarization of the Janus monolayer, the high degree of control over the internal dipole allows for the emulation of multi-level states. As shown in Supplementary Fig. 38, the MoSeS SP-FET effectively emulates artificial synaptic functions, including long-term potentiation (LTP), long-term depression (LTD), and spike-timing-dependent plasticity (STDP), while maintaining a high conductance (G) ratio, G_{min}/G_{max}. These findings underscore the potential of monolayer Janus materials as foundational elements for neuromorphic hardware, paving the way for more energy-efficient in-memory processing. Further work will be necessary to establish the switching mechanisms of the devices for advanced synaptic operation in addition to the memory function.

-Line 70,

“have shown promise as ferroelectric materials for non-volatile memory applications”

→ Replace with:

“have shown promise as polarization-based information storage materials for non-volatile memory applications”

-line 79

“ Semiconducting Ferroelectric FET (SFe)”

→ Replace with:

“switchable-polarization field-effect transistor (SP-FET)”

-line 144,

“ signifying the ferroelectric switching instead of charge trapping”

→ Replace with:

“ signifying the polarization switching instead of charge trapping”

-line 229,

“Janus MoSeS is a semiconducting ferroelectric monolayer in which polarization”

→ Replace with:

“Janus MoSeS is an n-type semiconducting monolayer in which polarization”

We thank the reviewer for this insightful suggestion. We agree that the 7-bit synaptic operation is a significant benchmark that highlights the high-performance capabilities of our Janus monolayer devices. Following the reviewer’s recommendation, we have substantially revised the Discussion section to better emphasize this result.

-line 362,

“DISCUSSION

We demonstrate a nonvolatile memory platform based on monolayer Janus MoSeS, exhibiting large memory windows, fatigue-free endurance, and long-term retention. Compared with conventional charge-trapping memories and previously reported ferroelectric layered semiconductors, the present device, operating through polarization-modulated conductance, demonstrates not only superior performance in terms of ultrafast switching and low-power operation but also offers distinct advantages in scalability and compatibility with modern field-effect transistor architectures. These results highlight the potential of semiconducting Janus monolayers for next-generation memory technologies.

We believe these revisions address the reviewer’s concerns and improve the clarity and balance of the manuscript.

Sincerely,

Seong Chu Lim

On behalf of all authors